INVESTIGATION OF DIFFERENCES BETWEEN FIELD AND LABORATORY pH MEASUREMENTS OF NATIONAL ATMOSPHERIC DEPOSITION PROGRAM/NATIONAL TRENDS NETWORK PRECIPITATION SAMPLES

NATALIE LATYSH and JOHN GORDON

U.S. Geological Survey, Denver, CO, U.S.A.

(* author for correspondence, e-mail: nlatysh@usgs.gov, Fax: 303 236 1880)

Abstract. A study was undertaken to investigate differences between laboratory and field pH measurements for precipitation samples collected from 135 weekly precipitation-monitoring sites in the National Trends Network from 12/30/1986 to 12/28/1999. Differences in pH between field and laboratory measurements occurred for 96% of samples collected during this time period. Differences between the two measurements were evaluated for precipitation samples collected before and after January 1994, when modifications to sample-handling protocol and elimination of the contaminating bucket o-ring used in sample shipment occurred. Median hydrogen-ion and pH differences between field and laboratory measurements declined from 3.9 μeq L^{-1} or 0.10 pH units before the 1994 protocol change to 1.4 μeq L^{-1} or 0.04 pH units after the 1994 protocol change. Hydrogen-ion differences between field and laboratory measurements had a high correlation with the sample pH determined in the field. The largest pH differences between the two measurements occurred for high-pH samples (>5.6), typical of precipitation collected in Western United States; however low-pH samples (<5.0) displayed the highest variability in hydrogen-ion differences between field and laboratory analyses. Properly screened field pH measurements are a useful alternative to laboratory pH values for trend analysis, particularly before 1994 when laboratory pH values were influenced by sample-collection equipment.

Keywords: measuring pH, NADP/NTN, precipitation pH, wet deposition monitoring

1. Introduction

Wet deposition is a major mechanism by which gaseous and particulate constituents are removed from the atmosphere and deposited on the Earth's surface, affecting aquatic and terrestrial systems (Hansen and Eatough, 1991; Nilles, 2000). Studying precipitation chemistry is vital in evaluating atmospheric composition, which is influenced by anthropogenic and natural sources (National Atmospheric Deposition Program, 1985; Munger and Eisenreich, 1983). Collection of precipitation samples for chemical analysis presents many challenges. The random occurrence of events and the dilute nature of precipitation enhance chances of contamination and add to the difficulty in achieving accurate analyses (Galloway and Likens, 1978). Onsite pH measurements are considered to be a more accurate assessment of precipitation chemistry than subsequent laboratory measurements

Figure 1. Map showing the 135 NADP/NTN sites that successfully met the data screening criteria for analysis of hydrogen ion differences between field and laboratory pH measurements for precipitation samples collected between 12/30/1986 and 12/28/1999.

(Hem, 1985). Differences between field and laboratory measurements have been observed for samples collected by monitoring networks and attributed to: (1) microbial metabolism of organic acids; (2) breakdown of particulate matter resulting in delayed neutralization of acid-contributing species (Bigelow *et al.*, 1989; Keene and Galloway, 1984; Chan *et al.*, 1987); and (3) other chemical changes that occur through transport, processing, and handling (Tang *et al.*, 1987; Gordon, 1999).

Differences between field and laboratory pH measurements consistently occur for weekly precipitation samples collected and analyzed by the National Atmospheric Deposition Program/National Trends Network (NADP/NTN) (National Atmospheric Deposition Program, 1994). Inspection of these pH differences is important because they are not uniform across the Nation. Bigelow *et al.* (1989) examined differences between field and laboratory pH measurements for NADP/NTN samples collected between 12/28/1983 and 01/04/1987. They discussed sample contamination associated with the bucket and lid used for sample collection, as well as seasonal and site-specific effects on the pH differences between field and laboratory measurements. The study discussed in this report examines differences between field and laboratory pH measurements for samples collected from 135 weekly precipitation-monitoring sites in the National Trends Network (NTN) for

the period from 12/30/1986 to 12/28/1999, during which changes to the NADP/NTN sample-handling protocol and within the atmospheric environment occurred (Figure 1).

Important changes to the NADP/NTN sample-handling protocol were implemented in 1994. Stringent limitations on sulfur dioxide emissions were phased in after the passage of the Clean Air Act Amendments in 1990, resulting in increasingly less acidic precipitation in some areas of the Nation. In this study, differences between laboratory and field pH measurements were examined before and after the 1994 protocol change. The influence on pH differences caused by: (1) changes in operational procedures, (2) changes in atmospheric chemistry due to reductions in sulfur dioxide emissions, and (3) physical characteristics such as site location, precipitation sample size, and hydrogen-ion concentration are all discussed in this report.

2. Material and Methods

2.1. BACKGROUND OF NADP/NTN

The NADP was initiated in 1978 by the Association of State Agricultural Experiment Stations to monitor long-term atmospheric chemistry and the effects pollutants have on aquatic and terrestrial systems (National Atmospheric Deposition Program, 1985; Nilles, 2000). The NTN is one of three networks that make up the NADP. As of February 2002, 236 sites were operating in the NADP/NTN. Analysis of precipitation samples is conducted by the Illinois State Water Survey, Central Analytical Laboratory (CAL), and includes the following constituents and properties: calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), potassium (K^+), sulfate (SO_4^{2-}), nitrate (NO_3^-), chloride (Cl^-), ammonium (NH_4^+), phosphorus (PO_4^{3-}), pH, and specific conductance (National Atmospheric Deposition Program, 1994). NADP/NTN precipitation samples are collected on a 7-day cycle, replacing the sample-collection bucket every Tuesday. Precipitation collected during the 7-day residence time in the collection bucket is analyzed as one composite sample. Because the NADP/NTN has a weekly sample-collection protocol, samples can have a minimum residence time of less than 1 day and a maximum residence time of 7 days, from the time the precipitation event occurs to the time the sample is collected. The NADP/NTN requires its site operators to make field measurements of pH and specific conductance.

By 1985, the CAL was supplying pre-tested, uniform-quality pH electrodes to a majority of the NADP/NTN sites (Gordon *et al.*, 1991). A quality-control check sample replicating typical precipitation is formulated by the CAL and provided to the NADP/NTN sites. Measuring the specific conductance and pH of the check sample prior to measuring the specific conductance and pH of the actual precipitation sample helps to identify potential problems. The precipitation samples are

shipped from the field to the CAL for a full suite of analyses, including laboratory pH and conductance measurements. The pH of precipitation can change over time from the inception of the precipitation event to the time that the pH is subsequently measured in the field and again at the laboratory; pH can even change during measurement. Laboratory pH values are commonly higher than field values. The United States Geological Survey (USGS) operates five external quality-assurance programs in support of the NADP/NTN to ensure the data are of high quality.

2.2. 1994 PROTOCOL CHANGE

Between 1978 and 1994, precipitation samples collected at NADP/NTN sites were shipped to the CAL in the sample-collection buckets. On 11 January 1994, the NADP/NTN changed sample shipping procedures; collection buckets are no longer used to ship precipitation samples to the CAL. Instead, the precipitation samples are decanted and mailed to the CAL in one-liter, wide-mouthed, High Density Polyethylene (HDPE) bottles. The sample shipping protocol was changed because the o-ring in the lid of the sample-collection bucket was found to contaminate samples by contributing the same ions present in precipitation, thus resulting in substantial differences between laboratory and field pH measurements for many sites (especially sites in the Western United States, where pH values tend to be greater than 4.8 (Lynch *et al.*, 1996). In separate studies, the CAL and the USGS examined the extent of contamination the o-ring contributed to each analyte (Gordon *et al.*, 1991; Nilles *et al.*, 1993; Lynch *et al.*, 1996).

2.3. DATA SCREENING

Field and laboratory analyses are performed on weekly precipitation samples, which are collected at NADP/NTN sites around the United States. If sample volume requirements are satisfied, NADP/NTN site operators perform pH and specific-conductance measurements in the field. Data included in this study were screened using the following criteria: data were derived only from NADP/NTN sites operating continuously from January 1987 through December 1999; of these sites, data were used only from those sites that successfully met the Intersite-Comparison Program goals (See *et al.*, 1990; Gordon, 1999) in at least 19 of 25 intersite-comparison studies conducted between 1987 and 1999; of these data, only data with codes 'w' or 'wa' assigned by the CAL, indicating sufficient sample volume for laboratory pH measurements, were included; and finally, data from laboratory and field pH values had to be available for a given data record. After all the screening steps were applied, data from 135 sites were included in the final analysis for this study.

The Intersite-Comparison Program is one of five external quality-assurance programs administered by the USGS for the NADP and is used to assess the accuracy of field measurements (See *et al.*, 1990; Gordon, 1999). Successful participation in semi-annual intersite-comparison studies, conducted from 1987 through 1999, was

used as a screening tool to help ensure that the field data being analyzed for this study were of good quality. In these studies, site operators were asked to determine the pH and specific conductance of synthetic precipitation check samples of composition unknown to them. These samples were formulated by the USGS and had pH and specific-conductance values similar to the wet-deposition samples collected by the NADP/NTN (Gordon, 1999). Requirement of successful participation in 19 intersite-comparison studies eliminated many sites from consideration because they had not participated in the NTN long enough to meet the criteria. Limiting the dataset to sites that were in operation during the entire study period ensures every site is equally represented in the dataset. Upon arrival at the CAL, precipitation samples are coded, specifying the condition of the sample. A code of 'w' indicates the sample volume is approximately 35 mL or greater. A code of 'wa' indicates the sample volume is less than 35 mL and requires dilution (Jane Rothert, Illinois State Water Survey, written commun., 2001). The code 'wa' was applied to less than 1% of the samples being considered in this study. A complete set of laboratory analyses is made on samples with validation codes of 'w' and 'wa' and only these samples are used by the NADP/NTN in calculating weighted-mean concentrations and depositions (National Atmospheric Deposition Program, 1994).

2.4. PRECIPITATION-WEIGHTED MEANS

The pH and the associated hydrogen-ion differences between laboratory and field measurements were evaluated for samples collected before and after the NADP/NTN protocol change. A total of 27 381 samples were included in the 1986–1994 dataset, and 25 063 samples were included in the 1994–1999 dataset. Precipitation-weighted mean concentrations were frequently used for the analyses presented in this report to reduce variability resulting from such influences as meteorological factors and to minimize bias due to outliers. Precipitation-weighted means were calculated using the following formula:

$$C_w = \frac{\sum_{i=1}^{n} [c_i P_i]}{\sum_{i=1}^{n} [P_i]} , \tag{1}$$

where C_w is the precipitation-weighted mean for a particular ion obtained for n samples, for the time period of interest. P_i and c_i are the precipitation depth, in millimeters (mm), and concentration of ionic species, in microequivalents per liter (μeq L^{-1}), respectively (National Atmospheric Deposition Program, 1994). When calculating hydrogen-ion precipitation-weighted means, pH values were converted to hydrogen-ion concentrations and expressed as microequivalents per liter. Use of the linearly scaled hydrogen-ion concentration values provides easier interpretation

TABLE I

Comparison of precipitation-weighted mean and median pH measurements made in the field and
in the laboratory between 1986 and 1999 using NADP/NTN precipitation samples

H_l^+/H_f^{+a}	n	%	PWM values[b]			Median values		
		samples	H_l^+/H_f^{+a}	pH laboratory	pH field	H_l^+/H_f^{+a}	pH laboratory	pH field
1986–1994								
>1	4602	16.8	1.49	4.62	4.70	1.10	4.44	4.5
<1	21862	79.8	0.70	4.95	4.75	0.71	4.86	4.65
=1	917	3.3	1.00	4.47	4.47	1.00	4.33	4.33
1994–1999								
>1	7179	28.6	1.99	4.81	4.91	1.12	4.66	4.73
<1	16722	66.7	0.78	4.93	4.81	0.83	4.82	4.72
=1	1162	4.6	1.00	4.63	4.63	1.00	4.47	4.47

[a] H_l^+/H_f^+ = Ratio of the hydrogen-ion concentration measured in the laboratory to the hydrogen-ion concentration measured in the field, calculated from pH measurements.
[b] PWM = Precipitation-Weighted Mean.

of the magnitude of change in concentration than pH, which is measured on a logarithmic scale (Park, 1987). Precipitation depths obtained from raingages rather than volumes derived from sample-collection buckets were used in this analysis because raingages tend to measure larger quantities and are considered to be more accurate (Galloway and Likens, 1978; National Atmospheric Deposition Program, 1994).

3. Results and Discussion

3.1. EFFECTS OF PROCEDURAL MODIFICATIONS

The median hydrogen-ion difference between field and laboratory measurements before the 1994 protocol change was 3.9 μeq L^{-1}. This difference provided a small shift in pH for precipitation samples with a field pH of 4.0 and a substantial shift in pH for samples with a field pH of 5.0. Table I shows the distribution of precipitation-weighted mean and median hydrogen-ion differences between field and laboratory measurements for the 1986–1994 and 1994–1999 datasets. Because extreme outliers influence calculation of the mean, precipitation-weighted mean values of pH are generally higher than median values. For the 1986–1994 dataset, laboratory pH measurements were higher than field values for 80% of

all samples; for the 1994–1999 dataset, the laboratory pH values were higher for 67% of all samples. Samples whose laboratory and field pH measurements were identical had the lowest median pH values in 1986–1994 and in 1994–1999 data-sets. A small difference between field and laboratory hydrogen-ion concentration in a low-pH sample may not be detectable by the pH monitoring equipment used by the NADP/NTN because of the relatively high hydrogen-ion concentration of the sample compared to the magnitude of the difference between the field and laboratory measurements.

The disparity between hydrogen-ion concentrations determined in the laborat-ory and field is shown by the H_l^+/H_f^+ ratio. A H_l^+/H_f^+ ratio of less than 1 signifies a lower field pH value than the subsequent laboratory pH measurement. The higher H_l^+/H_f^+ ratio for samples collected after the 1994 protocol change signifies smal-ler differences between laboratory and field pH measurements due to changes in sample-handling procedures.

Differences between laboratory and field pH measurements may affect inter-pretation of environmental impacts of hydrogen-ion deposition on ecological sys-tems, depending on which value is used in the evaluation. For example, precipita-tion collected at site NH02 (Hubbard Brook Experimental Forest) in 1999 had an average field pH of 4.49, yielding a total hydrogen-ion annual deposition of 0.39 kg ha^{-1}. A positive difference of 0.10 pH units would generate a total deposition of 0.31 kg ha^{-1}. Watershed 7 at the Hubbard Brook Experimental Forest covers an area of 76.4 ha. The difference of 0.08 kg ha^{-1} would translate into an annual difference of 5 kg of hydrogen-ion deposition over the Watershed 7 area. Depend-ing on the sensitivity of the system under investigation to hydrogen-ion input, this difference may prove significant.

At the website (http://nadp.sws.uiuc.edu/documentation/advisory.html), the CAL lists correction factors to adjust for o-ring influences on the hydrogen-ion concentrations for precipitation samples collected before the 1994 protocol change. Comparing the CAL results with the median differences calculated from the NADP/NTN data in this report, there is good agreement for samples with field pH values less than 5.6 (Table II). Due to elimination of the bucket o-ring, the median pH difference between field and laboratory measurements has decreased by 0.02 pH units and by 0.14 pH units for NADP/NTN precipitation samples with pH values less than 4.6 and with pH values between 4.6 and 5.6, respectively, collected after the 1994 protocol change. The median pH difference between field and laboratory measurements for NADP/NTN samples collected after the 1994 protocol change with field pH values greater than 5.6 has decreased by 0.21 pH units, whereas the CAL observed a greater difference (0.40–0.60 pH units).

3.2. SAMPLE pH AND ASSOCIATED HYDROGEN-ION DIFFERENCES

Other authors have also noted decreases in the hydrogen-ion concentration between precipitation samples analyzed in the field and those analyzed in the laboratory

TABLE II

Comparison of the o-ring effects on hydrogen-ion differences (μeq L^{-1}) and pH between field and laboratory pH measurements of NADP/NTN precipitation samples with results from the CAL study focusing on o-ring influences on sample chemistry

Field pH range	n 1987–1994	Median H$^+$ difference 1986–1994	Median pH difference 1986–1994	n 1994–1999	Median H$^+$ difference 1994–1999	Median pH difference 1994–1999	H$^+$ difference due to o-ring influence[a]	pH difference due to o-ring influence[b]	n used by the CAL for analyses	H$^+$ correction factors reported by CAL	pH correction factors reported by CAL
<4.6	13432	−5.71	0.05	10195	−2.85	0.03	2.86	0.02	112	3.2±1.1	0.03±0.01
4.6–5.6	12392	−3.60	0.20	13023	−1.30	0.06	2.30	0.14	191	2.5±0.5	0.13±0.02
>5.6	1557	−0.42	0.29	1845	−0.12	0.08	0.30	0.21	102	2.1±0.8	0.50±0.10

[a] H$^+$ difference due to o-ring influence was calculated by subtracting the median hydrogen-ion difference between field and laboratory pH measurements for NADP/NTN samples collected after the 1994 protocol change from the median hydrogen-ion difference for precipitation samples collected before the protocol change.
[b] pH difference due to o-ring influence was calculated by subtracting the median pH difference between field and laboratory measurements for NADP/NTN samples collected after the 1994 protocol change from the median pH difference for precipitation samples collected before the protocol change.
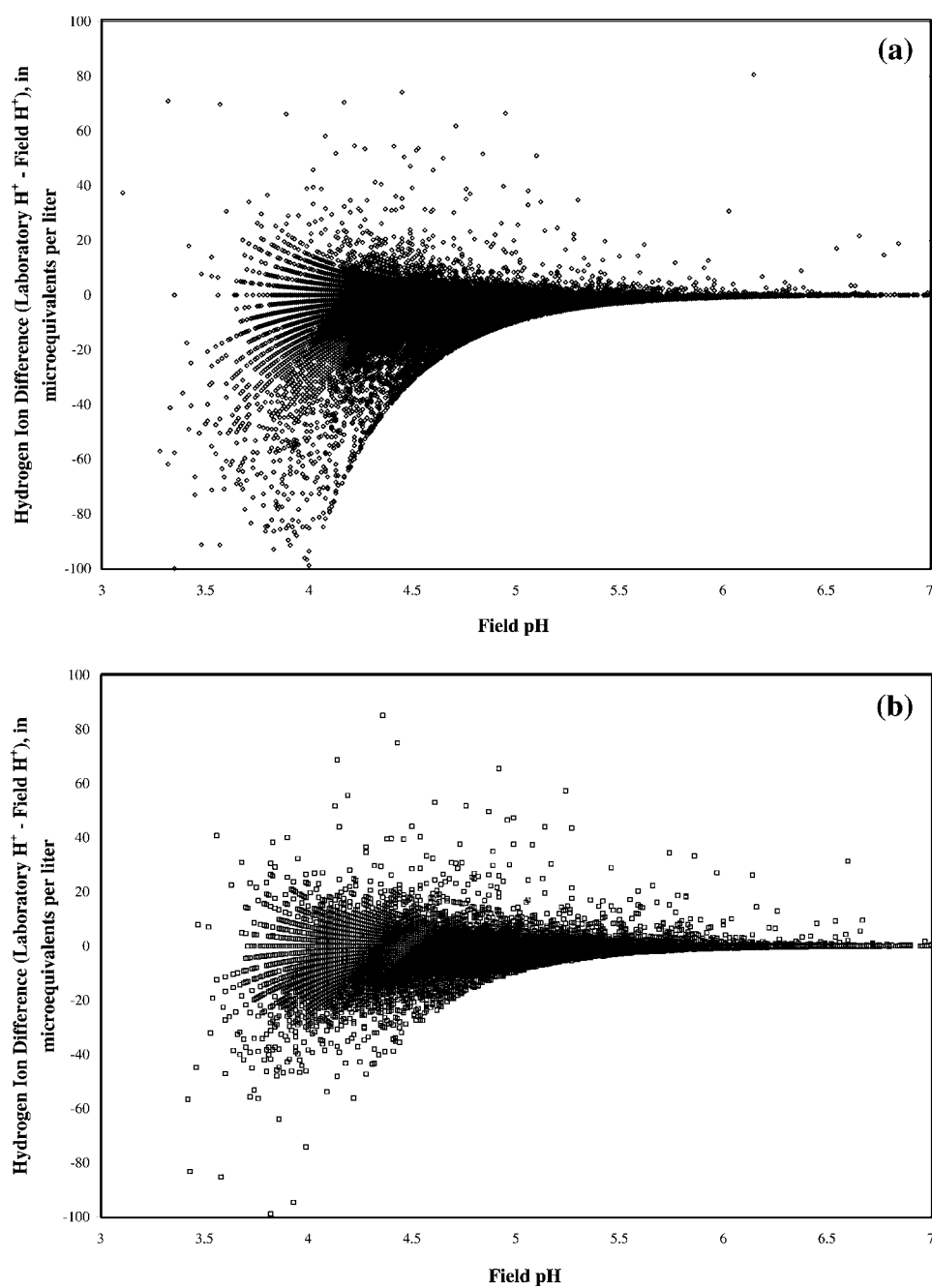
Figure 2. (a) Hydrogen-ion differences between laboratory and field pH measurements for NADP/NTN precipitation samples collected between 12/30/1986 and 01/04/1994 versus field pH. (b) Hydrogen-ion differences between laboratory and field pH measurements for NADP/NTN precipitation samples collected between 01/11/1994 and 12/28/1999 versus field pH.

(Keene and Galloway, 1984; Bigelow *et al*., 1989; Chan *et al*., 1987). The magnitude of the hydrogen-ion difference between a laboratory and field pH measurement is associated with the initial field pH measurement of the NADP/NTN precipitation sample, as shown in Figures 2a and b. While a majority of laboratory pH measurements are higher than the corresponding field pH measurements (previously discussed in Table I), some laboratory measurements are lower than corresponding field pH measurements for individual samples because the two measurements have uncertainties, which sometimes gives negative values for the difference (Gary Stensland, Illinois State Water Survey, written commun., 2002).

Low-pH solutions, generally pH of less than 5.0, exhibit a high degree of variability in hydrogen-ion differences. Hydrogen-ion differences between field and laboratory measurements decrease with increasing pH and become almost imperceptible in units of concentration for solutions whose field pH exceeds 6.0. The trend of decreasing hydrogen-ion differences between field and laboratory analyses with increasing pH values is similar for the 1986–1994 and 1994–1999 datasets. The smooth lower boundary of negative hydrogen-ion differences between field and laboratory measurements in Figures 2a and b reflects the maximum hydrogen-ion deficit that can occur between a field and a laboratory pH measurement. Difference in hydrogen-ion concentration between the two measurements cannot exceed the hydrogen-ion concentration determined during the field pH measurement. A 6.0 pH sample has a hydrogen-ion concentration of 1 μeq L^{-1}, whereas a 4.0 pH sample has a hydrogen-ion concentration of 100 μeq L^{-1}. The 4.0 pH sample can have greater variability of hydrogen-ion differences between field and laboratory pH measurements than the 6.0 pH sample, in units of concentration (μeq L^{-1}); however, low-pH samples will have smaller differences between field and laboratory values when the differences are measured in pH.

The logarithmic nature of the pH scale obscures some important attributes of the dataset. Figure 3 shows median pH differences between laboratory and field measurements for specific field pH ranges. The large hydrogen-ion differences of low-pH precipitation samples (pH < 4.6) are small compared to the large hydrogen-ion concentrations, resulting in minor pH differences between field and laboratory measurements both for the 1986–1994 and the 1994–1999 datasets. For solutions with pH values between 4.8 and 6.0, median pH differences before the protocol change were extremely large, ranging from 0.20 to 0.42 pH units. After the protocol change, median pH differences declined substantially to a range of 0.04 to 0.12 for the same pH range. The largest median pH differences occurred for solutions with pH ranges from 5.6 to 5.8, both in the 1986–1994 and the 1994–1999 datasets.

In the 1986–1994 dataset, the pH value measured in the laboratory exceeded the field pH measurement by more than 1.0 pH unit in 1184 of 27 381 samples. By comparison, in the 1994–1999 dataset, the laboratory pH measurement exceeded the field pH value by more than 1.0 standard pH unit in only 134 of 25,063 samples. While this large reduction of the number of samples with pH differences greater than 1.0 standard pH unit may be due in part to a reduction in measurement errors,
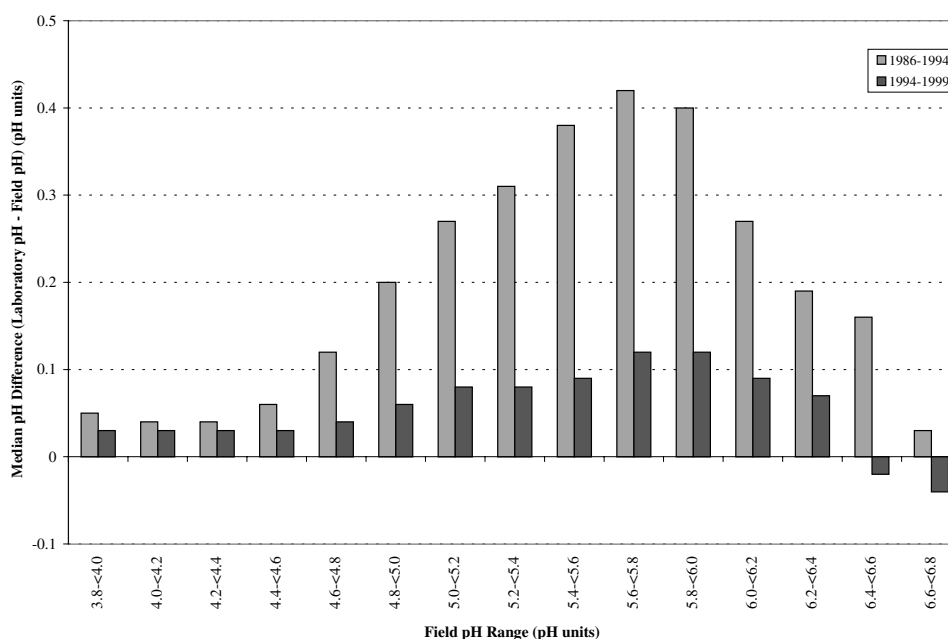
Figure 3. Median differences between laboratory and field pH measurements for specific field pH ranges measured on NADP/NTN precipitation samples between 12/30/1986 and 12/28/1999.

the elimination of the bucket o-ring likely explains most of this change. The contamination from the o-ring was highly variable and often significant in precipitation samples (See *et al.*, 1988; Nilles *et al.*, 1993; Gordon, 1999). Large pH differences between field and laboratory measurements may be due to a combination of other factors. A primary factor is contamination during sample handing, transport, and processing when hydrogen-ion differences may be influenced by surface chemistry, adsorption of ions to the shipping container walls (Gordon *et al.*, 1997), along with the previously discussed bucket o-ring influences. Other factors influencing pH differences include delayed neutralization of entrained particulates in the precipitation sample, measurement errors in the field or laboratory, and influences from organic acids.

Less than 3% of all NADP/NTN precipitation samples have pH values greater than 6.4. The median difference between laboratory and field hydrogen-ion concentrations for these samples is positive. This is not observed for data collected before the protocol change. Positive differences can result from introduction of additional hydrogen-ions between the field and laboratory pH measurements. Gain of hydrogen-ions may affect all samples; however, this effect is not seen until hydrogen-ion concentrations are low enough to exhibit these small positive differences. Positive hydrogen-ion differences were not seen in the 1986–1994 data because contamination from the bucket o-ring affected the hydrogen-ion concentration in the precipitation samples. The contamination was not uniform and varied
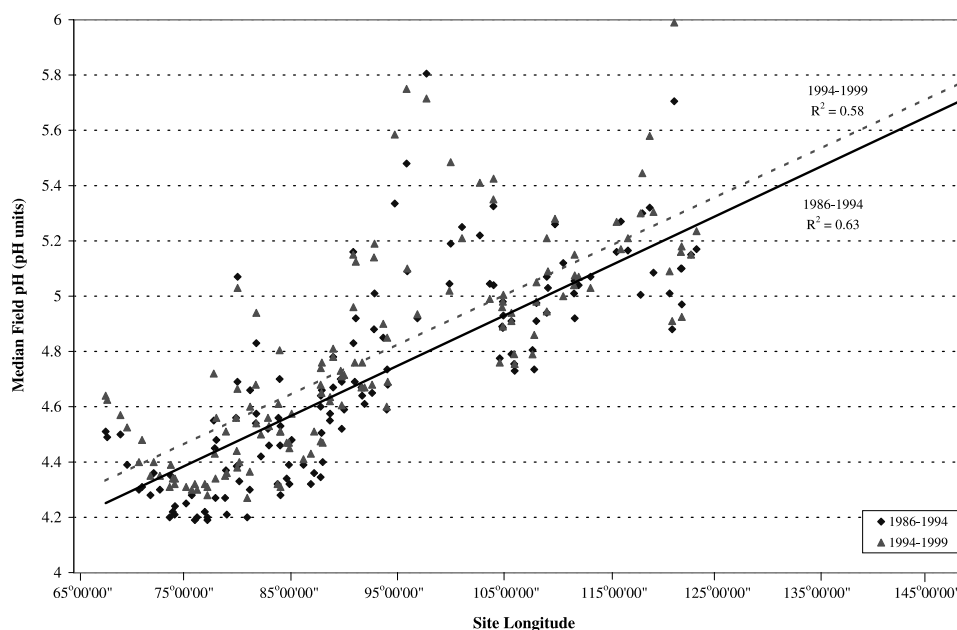
Figure 4. Median field pH versus site longitude for NADP/NTN sites collecting precipitation samples from 12/30/1986 to 12/28/1999. The equations of the least-squares regression lines are $y = 2e^{-06x} + 3.0197$ with $R^2 = 0.63$ for the 1986–1994 dataset (solid regression line), and $y = 2e^{-06x} + 3.1132$ with $R^2 = 0.58$ for the 1994–1999 dataset (dashed regression line).

by sample volume and pH (Lynch *et al.*, 1996). Small contributions to hydrogen-ion differences from other sources were obscured among the variability and large influences of the shipping, handling, processing, and bucket o-ring contamination on sample concentrations. Hydrogen-ion differences after the protocol change reflect influences from other sources that consistently affect all precipitation samples and are inherent to precipitation collection, such as sample size, sample pH and other site-specific factors, including climate, wind conditions, microbial activity, seasonal influences, availability of alkaline soils, snow cover, and vegetative cover (Bigelow *et al.*, 1989; Chan *et al.*, 1987). Because these factors are not uniform from site to site, inconsistencies in hydrogen-ion differences between laboratory and field pH values occur.

For the 1986–1994 dataset, the data were pooled and analyzed for each site, and a precipitation-weighted mean of the hydrogen-ion differences between field and laboratory measurements was determined. Using the same sites, the same analysis was performed for the 1994–1999 dataset. The data were trimmed to eliminate effects of extreme outliers, and the dataset was restricted to the 10th and 90th percentiles of these precipitation-weighted mean values. After trimming the dataset in this manner, the precipitation-weighted mean differences between laboratory and field hydrogen-ion measurements for the 135 individual NADP/NTN sites ranged from −6.39 to −1.20 μeq L^{-1} for the 1986–1994 dataset and from −3.51 to 0.13 μeq L^{-1}

for the 1994–1999 dataset. Median field pH increases with longitude (Figure 4), where the R^2 value is 0.63 for the 1986–1994 dataset and 0.58 for the 1994–1999 dataset. Precipitation acidity is highest in regions where anthropogenic emissions of acid anions (SO_2 and NO_x) are highest and concentrations of neutralizing soil components are lowest. Precipitation collected along the northern Atlantic coast and the lower Great Lakes region has the highest concentration of hydrogen ion, nitrate and sulfate (Munger and Eisenreich, 1983). The high concentrations of sulfate and nitrate associated with major urbanization, power production, industry and lack of abundant alkaline soils result in high ratios of acidic to neutralizing components (Munger and Eisenreich, 1983; Berner and Berner, 1996). This produces lower precipitation pH compared to the Western United States, inducing large hydrogen-ion differences. Conversely, high concentrations of basic cations, common to the Western United States (Munger and Eisenreich, 1983; Berner and Berner, 1996), generate large hydrogen-ion differences between field and laboratory measurements due to delayed neutralization of acidic species. Wind-blown soil dust is the major contributor of the acid neutralizing species Ca^{2+}, Mg^{2+} and K^+ to the atmosphere (Bigelow *et al.*, 1989; Munger and Eisenreich, 1983). High-pH values in the Midwestern United States are partly the result of an abundance of farmland without vegetative cover during the non-growing seasons; the barren farmland provides sources of calcareous soil dusts.

Precipitation-weighted mean hydrogen-ion differences between field and laboratory measurements declined for 119 of the 135 sites after the 1994 protocol change, due to elimination of the bucket o-ring which has eradicated large differences between laboratory and field pH measurements. Median field pH values are greater for 117 of the 135 sites in the 1994–1999 dataset than in the 1987–1993 dataset and median field pH values are unchanged for 5 of the 135 sites. Increasing field pH values may be due to the reduction of acidic deposition in the United States as dictated by the 1990 Clean Air Act Amendments that seek to lower acid-producing sulfur dioxide and nitrogen oxide emissions.

3.3. INFLUENCES OF BASIC CATIONS ON pH DIFFERENCES

Natural deterioration of rocks produces soil and dust, which are displaced into the atmosphere through wind erosion, agricultural practices, and vehicular traffic on unpaved roads (Gatz *et al.*, 1986; Tanner, 1990; Berner and Berner, 1996). Alkaline materials vary regionally, depending on soil type. Wind blown mineral particles can be transported for thousands of kilometers, resulting in high wet deposition of Ca^{2+} and neutralizing precipitation acidity (Munger and Eisenreich, 1983; Casado *et al.*, 1992; Carratala and Bellot, 1998; Berner and Berner, 1996; Gatz *et al.*, 1986; Ellis *et al.*, 1990). Disregarding non-neutralizing Mg^{2+} and Ca^{2+} containing compounds (e.g. $CaCl_2$), the concentrations of Mg^{2+} and Ca^{2+} must be equal to or greater than the hydrogen-ion difference between the laboratory and field measurements to be significant neutralizing constituents in NADP precipitation samples (Keene and
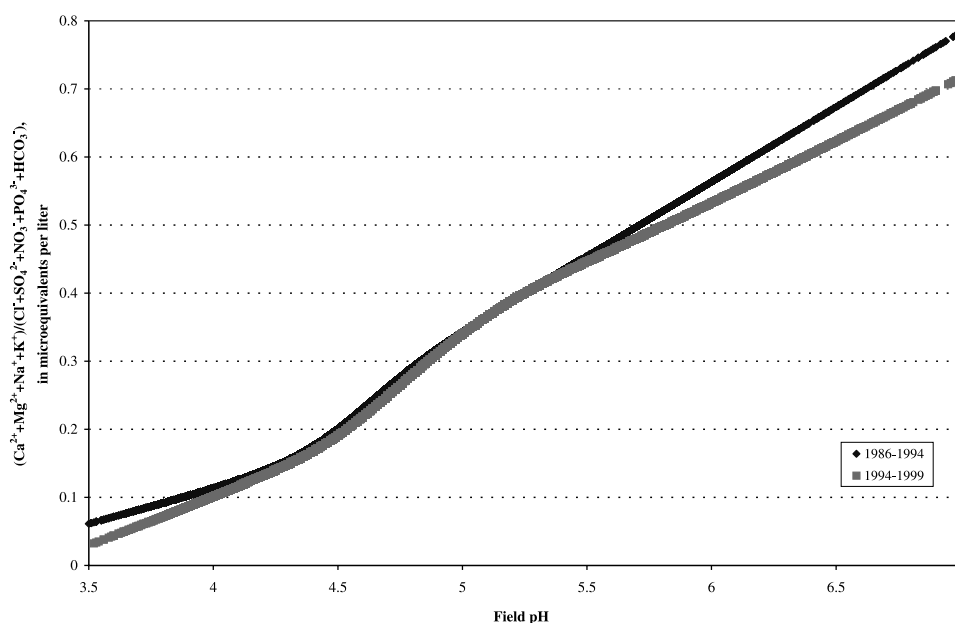
Figure 5. Smoothed frequency distribution for the 50th percentile using LOWESS (Locally Weighted Scatterplot Smoothing) Program of $(Ca^{2+} + Mg^{2+} + Na^+ + K^+)/(Cl^- + SO_4^{2-} + NO_3^- + PO_4^{3-} + HCO_3^-)$ ratio with field pH for NADP/NTN precipitation samples collected between 12/30/1986 and 12/28/1999.

Galloway, 1984; Chan *et al.*, 1987). Over 94% of the precipitation samples had larger combined concentrations of Mg^{2+} and Ca^{2+} than hydrogen-ion differences (in $\mu eq\ L^{-1}$), before and after the protocol change. High hydrogen-ion concentration promotes the dissolution of carbonate materials and neutralization of free acidity, which can contribute to large hydrogen-ion differences between laboratory and field measurements. Low- and high-pH NADP/NTN samples have high concentrations of Ca^{2+} and Mg^{2+}. The smallest median $Ca^{2+} + Mg^{2+}$ concentrations, less than 6.0 $\mu eq\ L^{-1}$, were found for solutions with a pH range of 4.7 to 5.2. Dissolution of carbonate minerals increases with decreasing values for solution pH, resulting in high concentration of basic cations (Stumm and Morgan, 1996). However, the ratio of basic cations to anions was not high enough to elevate the solution pH, shown as the Locally Weighted Scatterplot Smoothing (LOWESS) for the 1986–1994 and 1994–1999 datasets in Figure 5. Elevated concentrations of basic cations in high-pH solutions neutralize acidic components. Precipitation samples with high-pH values (>5.6) have high ratios of basic cations to acidic anions resulting in high pH values. The precipitation-weighted mean ratio both for the 1986–1994 and the 1994–1999 datasets of $(Ca^{2+} + Mg^{2+} + K^+ + Na^+)/(Cl^- + SO_4^{2-} + NO_3^- + HCO_3^- + PO_4^{3-})$ for high-pH solutions (field values >5.6) was 0.6, whereas for solutions with pH values less than 5.6 the ratio was 0.3.
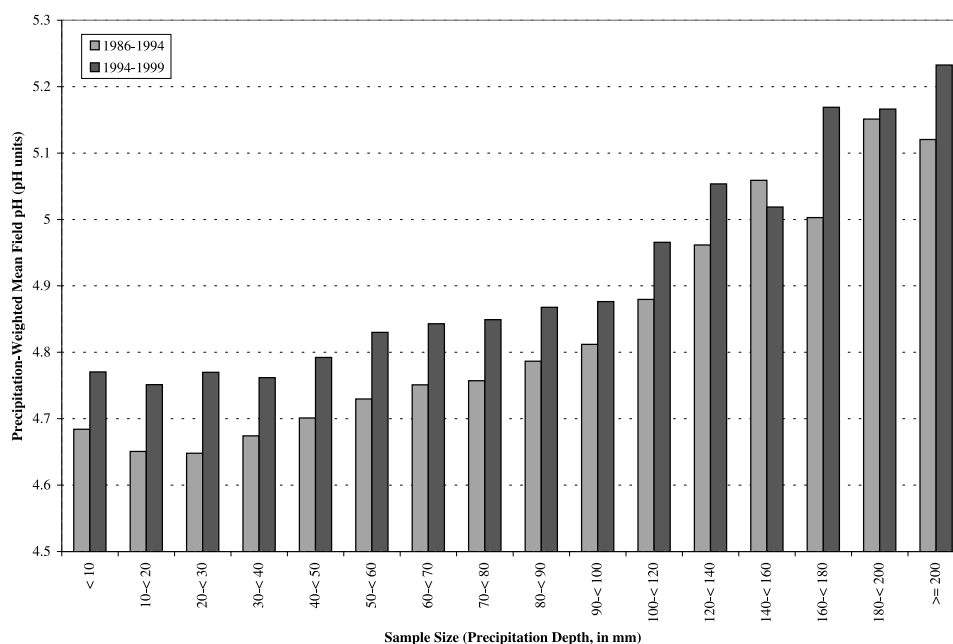
Figure 6. Comparison of precipitation-weighted mean field pH with size of NADP/NTN precipitation sample collected between 12/30/1986 and 12/28/1999.

For the small number of samples where the combined Mg^{2+} and Ca^{2+} concentration did not exceed the hydrogen-ion difference, other factors such as sample handling and oxidation of organic acids most likely play a part, as Keene and Galloway (1984) report. The rate at which microbes metabolize organic acids depends on temperature, microbial population, and availability of nutrients and energy sources (Keene and Galloway, 1984). Consumption of formic and acetic acids by microbes occurs quickly and falls off exponentially following a precipitation event (Jane Rothert, Illinois State Water Survey, written commun., 2001). Consumption of formic and acetic acids may be important reactions in reducing the hydrogen-ion concentration between the period of time that field measurements and laboratory measurements are completed.

3.4. INFLUENCES OF PRECIPITATION AMOUNT ON pH

Rainout and washout are the two main physical processes influencing precipitation chemistry. Rainout involves in-cloud scavenging by condensation and nucleation of cloud droplets. Washout involves reactions of water droplets with atmospheric gases and particulates during their descent from the cloud base to the ground (Schroder *et al.*, 1987). As a storm progresses, cloud droplets grow through coalescence with other droplets and nucleation, thus decreasing ionic concentrations. Similarly, the washout process decreases ionic concentrations in the lower atmosphere,

changing pH. Precipitation amount and frequency of events influence precipitation chemistry because brief events are washout dominated (Munger and Eisenreich, 1983; Durand *et al.*, 1992; Jordan *et al.*, 1995; Berner and Berner, 1996; Lee *et al.*, 2000), and an initial precipitation sample typically has the highest ionic concentration (Schroder *et al.*, 1987). Increasing pH with increasing precipitation amount is observed both in the 1986–1994 pre-protocol change period of the NADP/NTN and in the 1994–1999 post-protocol change period, which might be explained by rainout and washout processes (Figure 6). It is worth noting that NADP/NTN precipitation samples collected on a weekly basis are likely to sample more than one event. Large weekly sample volumes reflect either frequent events during the preceding week or one or more large events.

It appears that the initial pH, determined in the field, is the dominant factor controlling hydrogen-ion concentration differences between field and laboratory measurements, based on the analysis of results from a large number of Eastern and Western United States sites. Precipitation samples with initially higher pH values in the field (pH > 4.6) experienced greater laboratory-field pH differences than samples with pH < 4.6. Precipitation amount appears to be a secondary influence on hydrogen-ion concentration differences between field and laboratory measurements. This conclusion was determined by examining the pH of precipitation samples included in the 1994–1999 dataset, collected from 15 Western United States sites (precipitation-weighted mean pH range: 5.30–6.04) and from 15 Eastern United States sites (precipitation-weighted mean pH range: 4.31–4.45). Hydrogen-ion differences between field and laboratory measurements ranged from –11.30 to 5.81 μeq L^{-1} for the Eastern sites and from –4.16 to 1.61 μeq L^{-1} for the Western sites, at the 10th and 90th percentiles, respectively. Results from a small number of representative sites from this larger analysis are shown by way of example. The Western sites, WA24 and OR18, were chosen because they have similar precipitation-weighted mean pH values (5.26 and 5.32, respectively) and median precipitation sample sizes (12.19 and 11.18 mm, respectively). PA42 and OH49 were chosen as the Eastern sites because they also have similar precipitation-weighted mean pH values (4.38 and 4.31, respectively) and median precipitation sample sizes (18.8 and 21.59 mm, respectively), although the precipitation-weighted mean pH values are lower and median sample sizes higher than those of the two Western sites. Figures 7a and b show hydrogen-ion differences between field and laboratory measurements for samples collected from the four sites between 1994 and 1999. Hydrogen-ion differences were larger and more variable for smaller sample sizes. However, the Eastern sites, PA42 and OH49, which generally have precipitation of lower pH, had larger hydrogen-ion differences between field and laboratory measurements than the Western sites, WA24 and OR18, for similar sample sizes. Hydrogen-ion differences for precipitation samples collected from these Western sites ranged from –4.00 to 1.33 μeq L^{-1} and from –11.21 to 13.27 μeq L^{-1} for samples collected from the two Eastern sites, at the 10th and 90th percentiles, respectively.
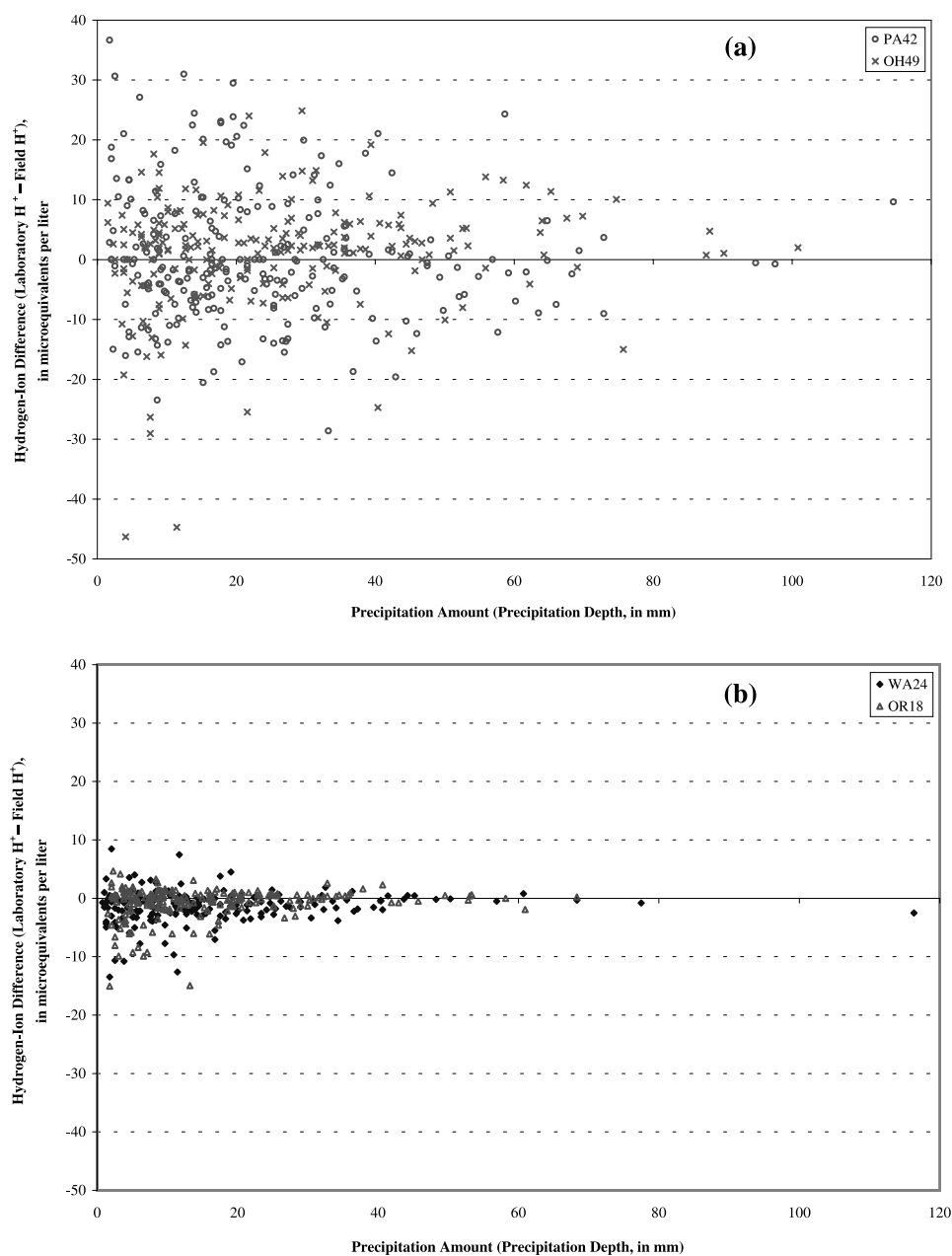
Figure 7. (a) Hydrogen-ion differences between field and laboratory measurements for different precipitation sample sizes collected from NADP/NTN sites PA42 and OH49 between 01/11/1994 and 12/28/1999. (b) Hydrogen-ion differences between field and laboratory measurements for different precipitation sample sizes collected from NADP/NTN sites WA24 and OR18 between 01/11/1994 and 12/28/1999.
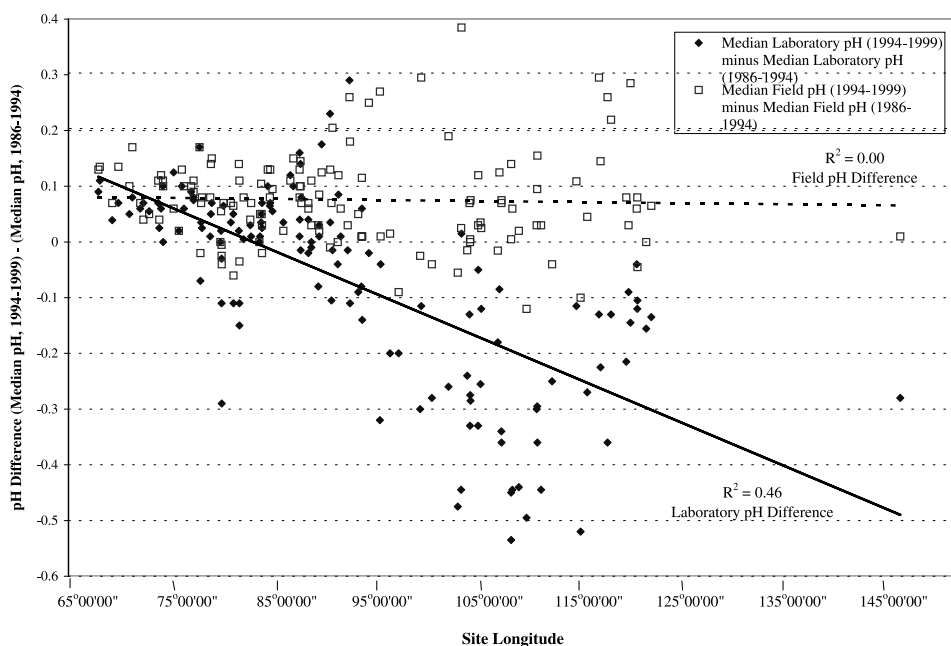
Figure 8. Comparison of site longitude and pH differences for field and laboratory measurements conducted before and after the 1994 protocol change. The equations of the least-squares regression lines are $y = -8e^{-07x} + 0.6294$ with $R^2 = 0.46$ for the median laboratory differences (solid regression line), and $y = -2e^{-08x} + 0.0934$ with $R^2 = 0.00$ for the median field differences (dashed regression line).

The precision of measuring hydrogen-ion concentration varies with pH. The difficulty of measuring pH was assessed by analyzing results from 25 intersite-comparison studies conducted from 1987 to 1999. An assessment of pH values reported for the synthetic check samples by participating site operators indicates that the interquartile range increased with increasing median values for pH in each study, reflecting the increased difficulty of precisely measuring higher pH solutions, a conclusion also noted by Gordon *et al.* (1991). Therefore, the larger hydrogen-ion differences between field and laboratory measurements for the lower pH samples collected from the two Eastern United States sites, OH49 and PA42, are most likely attributed to the variability of hydrogen-ion differences inherent to low-pH samples rather than error due to difficulty measuring low-pH precipitation samples.

3.5. pH DIFFERENCES BEFORE AND AFTER THE 1994 PROTOCOL CHANGE

Differences between median laboratory and field pH values were examined for each site before and after the 1994 protocol change to discern changes as a result of procedural modifications and reduction of atmospheric species contributing to precipitation acidity. Differences in median field pH values for each of the 135
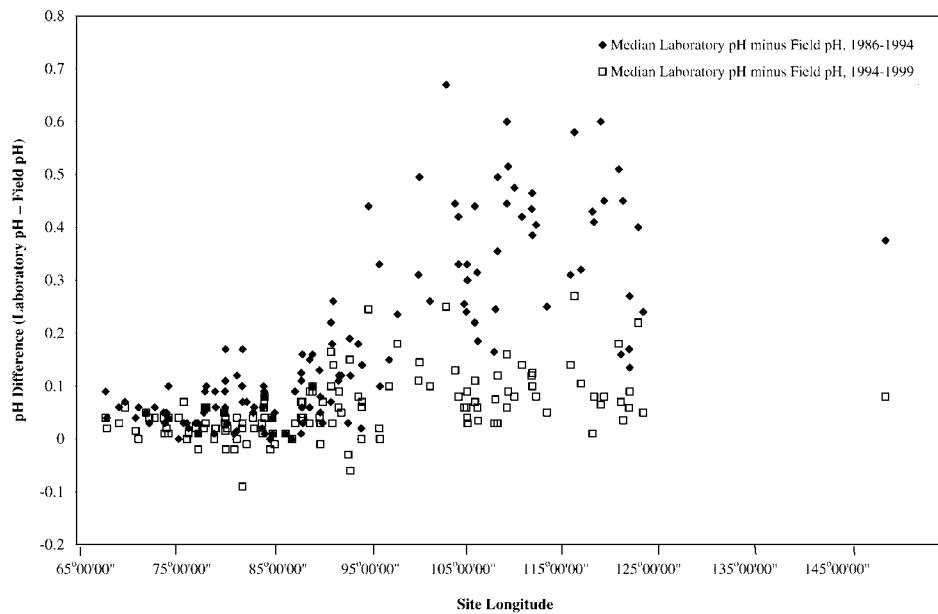
Figure 9. Median differences between laboratory and field pH measurements for NADP/NTN precipitation samples collected between 1986 and 1994 and for samples collected between 1994 and 1999.

sites before and after the 1994 protocol change are not equivalent to the median laboratory pH differences (Figure 8). Of the 135 sites, 112 showed higher median field pH values in the 1994–1999 dataset than in the 1986–1994 dataset, whereas 62 of the sites showed higher median laboratory pH values in the 1994–1999 dataset than in the 1986–1994 dataset. With one exception, all sites located in the Western United States (west of $100°00'00''$ longitude, mid-Nebraska) showed lower median laboratory pH values after the 1994 protocol change, while a majority of all sites showed increased median field pH values.

Positive field and negative laboratory pH differences for sites at a longitude west of $100°00'00''$ (mid-Nebraska) indicated that pH differences between field and laboratory values have decreased because laboratory measurements no longer tend to overestimate sample pH. Before the 1994 protocol change, laboratory analyses overestimated the pH substantially for Western sites (Figure 9), erroneously demonstrating that precipitation pH was higher than precipitation pH values measured subsequent to the 1994 protocol change. Differences between field and laboratory measurements decreased substantially after the 1994 protocol change. Comparison of median laboratory pH values measured before and after the protocol change erroneously implies declining pH in precipitation from Western United States sites. Laboratory pH measurements have always been high-quality measurements, necessary for ion balance and quality-control checks. Field pH values

are more representative of actual hydrogen-ion concentration in precipitation at the time of the event. While field pH values were not biased by sampling apparatus before the 1994 protocol change, caution must be exercised when using laboratory pH values before 1994 for trend analysis because of the previously discussed changes in sample chemistry during shipping and processing of the samples from the field to the laboratory.

4. Conclusions

Hydrogen-ion differences between field and laboratory analyses have decreased substantially for NADP/NTN precipitation samples collected since the 1994 protocol change, which eliminated shipment of samples in 14-L collection buckets that introduced the same ions present in precipitation. Differences in pH between field and laboratory analyses are greatest for high-pH samples. Hydrogen-ion differences between field and laboratory measurements correlate with the initial hydrogen-ion concentration. Sample size, precipitation frequency, neutralization of hydrogen-ion by $CaCO_3$ and $MgCO_3$, and degradation of organic acids may also influence pH differences between field and laboratory measurements. Smaller precipitation samples and infrequent precipitation events may result in increased pH variability between field and laboratory measurements. The variability of hydrogen-ion differences between field and laboratory measurements precludes use of a correction factor applied to laboratory pH values to make them commensurate with field pH values. Laboratory determinations of pH were significantly larger than the corresponding field measurements made before 1994 when the sample-shipping protocol was changed for the NADP/NTN. Field pH measurements remain useful for determining the precipitation chemistry prior to changes that affect sample chemistry between the field and laboratory measurements because laboratory measurements continue to overestimate the pH, and therefore, underestimate the hydrogen-ion concentration at the time of sample collection: 67% of the precipitation samples collected between 1994–1999 had a higher laboratory than field pH value. Between 1986 and 1994, 80% of the precipitation samples had a laboratory pH value that was higher than the field pH value. While high-quality laboratory pH values are valuable for many purposes, the use of laboratory pH values for analysis of precipitation pH trends before 1994 may produce erroneous results due to bias introduced by contamination from the bucket o-ring, particularly in the Western United States where the use of laboratory pH values for long-term analyses implies decreasing pH over time. As values for precipitation pH increase in many parts of the United States due to emission reductions, differences between field and laboratory pH measurements are expected to increase, somewhat reflecting the tendency for laboratory-field pH differences to increase with increasing values for sample pH.

References

Berner, E. K. and Berner, R. A.: 1996, *Global Environment: Water, Air, and Geochemical Cycles*, Prentice Hall, New Jersey, pp. 62–140.

Bigelow, D. S., Sisterson, D. L. and Schroder, L. J.: 1989, 'An interpretation of differences between field and laboratory pH values reported by the National Atmospheric Deposition Program/National Trends Network Monitoring Program', *Environ. Sci. Technol.* **23**, 881–887.

Carratala, A. and Bellot, J.: 1998, 'Neutralization of nitrate and sulphate in precipitation on the eastern mediterranean coast of Spain. Implications for acidification risk', *Water, Air, and Soil Pollut.* **104**, 237–257.

Casado, H., Encinas, D. and Lacaux, J. P.: 1992, 'The moderating effect of the Ca^{2+} ion on the acidity in precipitation (short communication)', *Atmos. Environ.* **26A**, 1175.

Chan, W. H., Tang, A. J. S., Chung, D. H. S., and Reid, N. W.: 1987, 'An analysis of precipitation chemistry measurements in Ontario', *Environ. Sci. Technol.* **21**, 1219–1224.

Durand, P., Neal, C. and Lelong, F.: 1992, 'Anthropogenic and natural contributions to the rainfall chemistry of a mountainous area in the Cevennes National Park (Mont-Lozere, Southern France)', *J. Hydrology* **130**, 71–85.

Ellis, E. C., Erbes, R. E. and Grott, J. K.: 1990, 'Abatement of Atmospheric Emissions in North America: Progress to Date and Promise for the Future', in S. E. Lindberg, A. L. Page and S. A. Norton (eds), *Acidic Precipitation, Vol. 3: Sources, Deposition, and Canopy Interactions*, Springer-Verlag, New York, pp. 285–322.

Galloway, J. N. and Likens, G. E.: 1978, 'The collection of precipitation for chemical analysis', *Tellus* **30**, 71–82.

Gatz, D. F., Barnard, W. R. and Stensland, G. J.: 1986, 'The role of alkaline materials in precipitation chemistry: A brief review of the issues', *Water, Air, and Soil Pollut.* **30**, 245–251.

Gordon, J. D.: 1999, 'External Quality-Assurance Results for the National Atmospheric Deposition Program/National Trends Network, 1995–1996', *U.S. Geological Survey Water-Resources Investigations Report 99-4072*, pp. 69.

Gordon, J. D., Willoughby, T. C. and Schroder, L. J.: 1991, 'Summary of the National Atmospheric Deposition Program/National Trends Network Intersite-Comparison Program, November 1978–November 1989', *U.S. Geological Survey Water-Resources Investigations Report 91-4061*, pp. 26.

Gordon, J. D., Nilles, M. A., Polacsek, D. K. and Ratcliff, M. E.: 1997, 'External Quality-Assurance Results for the National Atmospheric Deposition Program/National Trends Network During 1994', *U.S. Geological Survey Water-Resources Investigations Report 97-4201*, pp. 42.

Hansen, L. D. and Eatough, D. J.: 1991, *Organic Chemistry of the Atmosphere*, CRC Press, Boston, pp. 233–284.

Hem, J. D.: 1985, 'Study and Interpretation of the Chemical Characteristics of Natural Water', *U.S. Geological Survey Water-Supply Paper 2254*, pp. 64–66.

Jordan, T. E., correll, D. L., Weller, D. E. and Goff, N. M.: 1995, 'Temporal variation in precipitation chemistry on the shore of the Chesapeake Bay', *Water, Air, and Soil Pollut.* **83**, 263–284.

Keene, W. C. and Galloway, J. N.: 1984, 'Organic acidity in precipitation of North America', *Atmos. Environ.* **18**, 2491–2497.

Lee, B. K., Hong, S. H. and Lee, D. S.: 2000, 'Chemical composition of precipitation and wet deposition of major ions on the Korean Peninsula', *Atmos. Environ.* **34**, 563–575.

Lynch, J. A., Bowersox, V. C. and Grimm, J. W.: 1996, 'Trends in Precipitation Chemistry in the United States, 1983–1994: An Analysis of the Effects in 1995 of Phase I of the Clean Air Act Amendments of 1990, Title IV', *U.S. Geological Survey Open-File Report 96-0346*, pp. 19.

Munger, J. W. and Eisenreich, S. J.: 1983, 'Continental-scale variations in precipitation chemistry. Ion concentrations are dominated by land use and proximity to man-made emissions', *Environ. Sci. Technol.* **17**, 32–42.

National Atmospheric Deposition Program: 1985, *NADP/NTN Annual Data Summary, Precipitation Chemistry in the United States, 1982*, Natural Resource Ecology Laboratory, Colorado State University, Fort Collins, pp. 135.

National Atmospheric Deposition Program: 1994, *NADP/NTN Annual Data Summary, Precipitation Chemistry in the United States, 1993*, Natural Resource Ecology Laboratory, Colorado State University, Fort Collins, pp. 465.

Nilles, M. A.: 2000, 'Atmospheric Deposition Program of the U.S. Geological Survey', *USGS Fact Sheet 112-00*.

Nilles, M. A., Gordon, J. D., Willoughby, T. C. and Schroder, L. J.: 1993, 'External Quality-Assurance Results for the National Atmospheric Deposition Program/National Trends Network During 1990', *U.S. Geological Survey Open-File Report 92-4101*, pp. 33.

Park, C. C.: 1987, *Acid Rain: Rhetoric and Reality*, Methuen, New York, pp. 23–25.

Schroder, L. J., Brooks, M. H., Garbarino, J. R. and Willoughby, T. C.: 1987, 'The Influence of an Urban Environment in the Chemical Composition of Precipitation', in R. C. Averett and D. M. McKnight (eds), *Chemical Quality of Water and the Hydrologic Cycle*, Lewis Publishers, Inc., Michigan, pp. 40–53.

See, R. B., Schroder, L. J. and Willoughby, T. C.: 1988, 'External Quality-Assurance Results for the National Atmospheric Deposition Program/National Trends Network During 1986', *U.S. Geological Survey Water-Resources Investigations Report 88-4007*, pp. 15.

See, R. B., Willoughby, T. C., Brooks, M. H. and Gordon, J. D.: 1990, 'Programs and Analytical Methods for the U.S. Geological Survey Acid Rain Quality-Assurance Project', *U.S. Geological Survey Water-Resources Investigations Report 90-4029*, pp. 57.

Stumm, W. and Morgan, J. J.: 1996, *Aquatic Chemistry*, John Wiley & Sons, New York, pp. 186, 236.

Tang, A. J. S., Chan, W. H., Orr, D. B., Bardswick, W. S. and Lusis, M. A.: 1987, 'An evaluation of the precision, and various sources of error, in daily and cumulative precipitation chemistry sampling, *Water, Air, and Soil Pollut.* **36**, 91–102.

Tanner, R.: 1990, 'Sources of Acids, Bases, and their Precursors in the Atmosphere', in S. E. Lindberg, A. L. Page and S. A. Norton (eds), *Acidic Precipitation, Vol. 3: Sources, Deposition, and Canopy Interactions*, Springer-Verlag, New York, pp. 1–19.